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Charles H. Drummond III
Ohio State University
Columbus, Ohio

and

Narottam P. Bansal
Lewis Research Center
Cleveland, Ohio

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PHASE TRANSFORMATIONS IN $SrAl_2Si_2O_8$ GLASS

Charles H. Drummond, III
Department of Materials Science and Engineering
The Ohio State University
Columbus, OH 43210

and

Narottam P. Bansal
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, OH 44135

SUMMARY

Bulk glass of $SrAl_2Si_2O_8$ composition crystallized at temperatures below 1000 °C into hexacelsian, a hexagonal phase which undergoes a reversible, rapid transformation to an orthorhombic phase at 758 °C, and at higher temperatures crystallized as celsian, a monoclinic phase. The glass transition temperature and the crystallization onset temperature were determined to be 883 °C and 1086 °C, respectively, from DSC at a heating rate of 20 °C/min. Thermal expansion of the various phases and density and bend strengths of cold isostatically pressed glass powder bars, sintered at various temperatures, were measured. The kinetics of the hexacelsian-to-celsian transformation for $SrAl_2Si_2O_8$ were studied. Hexacelsian flakes were isothermally heat treated at temperatures from 1025-1200 °C for various times. Avrami plots were determined by quantitatively measuring the amount of monoclinic celsian formed at various times using XRD. The Avrami constant was determined to be 1.1, suggesting a diffusionless, one-dimensional transformation mechanism. The activation energy was determined from an Arrhenius plot of ln k vs. $1/T$ to be 125 kcal/mole. This value is consistent with a mechanism which transforms the layered hexacelsian structure to a three-dimensional framework celsian structure and involves the breaking of Si-O bonds.

INTRODUCTION

Composite materials that exhibit structural stability and strength at high temperatures are required for improved propulsion systems and as structural materials for aerospace applications. The low thermal expansion matrix phase in such composites must also be stable in oxidizing environments. Additional requirements are a moderate strength at temperatures in excess of 1500 °C and maintenance of that strength during cycling to these temperatures. The development of a high-temperature glass-ceramic matrix reinforced with high modulus fibers may meet these requirements.

One such material being considered for the high-temperature matrix component of the composite is the mineral celsian, $BaAl_2Si_2O_8$, with a melting point of 1760 °C. Two polymorphs of $BaAl_2Si_2O_8$ exist -- a monoclinic phase, celsian, and a high-temperature hexagonal phase, hexacelsian. Unfortunately, the hexagonal phase exists as a metastable phase at all temperatures which are below the equilibrium transformation temperature of 1590 °C. The transformation to the monoclinic phase from the hexagonal phase is very sluggish. Hexacelsian exhibits a reversible structural transformation into an orthorhombic phase at ≈300 °C, accompanied by a large volume change, which makes it unsuitable as a matrix material for high-temperature structural applications[1].

The strontium analogue, $SrAl_2Si_2O_8$, readily transforms to the celsian structure, and exhibits the same degree of refractoriness, making it more attractive as a matrix material. The objectives of the present work were to study the phase transformations occurring in a glass of $SrAl_2Si_2O_8$ composition on heat treatment and also to investigate the kinetics of the phase transformation of the hexacelsian to the celsian structure.

EXPERIMENTAL METHODS

Glass of stoichiometric composition, $SrAl_2Si_2O_8$, (SAS), was melted[2] at ≈2100-2200 °C in a continuous electric melter with Mo electrodes using laboratory grade $SrCO_3$, Al_2O_3, and SiO_2. Flakes and powder were produced with an as-melted composition (wt%) of 33.7 SrO, 31.5 Al_2O_3, 33.8 SiO_2, 0.12 Na_2O, 0.86 BaO, and 0.01 MoO_3. The Ba, Sr, Al, and Si contents were determined by wet chemical analysis and Mo by spectrographic technique.

Heat treatments of the glass were carried out in air using a programmable Lindberg box furnace with temperature control of better than ±5 °C of the set value. The glass powder was uniaxially cold-pressed at 5,000 psi into 7.9 x 5.5 x 55 mm rectangular bars and sintered at various temperatures. Some bars were cold isostatically pressed (CIP) at 60,000 psi and hot isostatically pressed (HIP) at 1350 °C for 4 h under 45,000 psi argon gas.

Density (ρ) and 3-point flexural strength (σ) of glass powder bars, sintered at various temperatures, were measured. The glass transition (T_g) and crystallization onset (T_c) temperatures were determined by differential scanning calorimetry (DSC). The liquidus and crystallization temperatures from the melt were measured using high temperature DTA. The linear thermal expansion coefficient (α) was determined using a Perkin-Elmer thermal mechanical analyzer TMA-7.

The weight fraction of the celsian formed from pure hexacelsian flakes by isothermal heat treatments from 1025-1200 °C for various times was quantitatively determined using x-ray diffraction (XRD). Reference standards were prepared by mixing pure hexagonal and monoclinic phases in different ratios. The peak areas of two monoclinic XRD peaks (2θ = 27.2 and 27.6°), which did not overlap with the hexagonal peaks, were measured and a calibration curve determined. XRD scans were run in triplicate on each standard sample for the calibration curve and the various heat treated samples.

RESULTS AND DISCUSSION

The liquidus measured was 1660 °C and T_c from the melt ≈1450 °C. These values are in reasonable agreement with those of Talmy and Haught[3]. Thus, the melt is supercooled at a quench rate of 20 °C/min in the DTA by ≈200 °C before crystallization of the monoclinic phase. The activation energy for the crystallization of the SAS glass was previously reported[4] as 450 kJ/mole with an Avrami constant of 1.4. The addition of Ba favors the crystallization of hexacelsian[2].

A series of DSC scans for the SAS glass is shown in Figure 1. A sample of the bulk glass was heated at 20 °C/min to 1300 °C in argon and fast quenched in the DSC. The T_g was 883 °C, and the crystallization to hexacelsian occurred at 1086 °C. When the quenched sample was reheated (second run), an endothermic peak for the orthorhombic to hexagonal

phase transformation appeared with an onset temperature of 758 °C. This was significantly higher than the transformation temperature of 300 °C for the barium analogue. At some higher temperature, the hexacelsian transformed to celsian, but no thermal event corresponding to this transformation appeared in the DSC scan. From 1300 °C the specimen was fast quenched to room temperature again in the DSC. On reheating (third run) this quenched sample, the peak corresponding to the orthorhombic to hexagonal structural change was absent, indicating that the hexacelsian had already transformed to celsian during the second run. These results were further verified by XRD of the DSC samples. The increase in the orthorhombic-to-hexagonal transformation temperature from 300 °C in the Ba analogue to 758 °C may be related to the increased stability of the celsian structure of the Sr analogue.

The α for the monoclinic phase was determined by TMA to be 2.7×10^{-6}/°C (20-800 °C), orthorhombic 5.4×10^{-6}/°C (20-600 °C) and hexagonal 11.1×10^{-6}/°C (800-900 °C). The corresponding values determined[5] from dilatometry are 7.6×10^{-6}/°C (30-500 °C) for the orthorhombic and 7.5×10^{-6}/°C (700-1000 °C) for the hexagonal phases. The reason for the difference in α values from this study and the literature values is not clear. For composite applications, the lower expansion of the monoclinic phase is usually desirable.

The density, phases formed and the bend strengths of various samples sintered at various temperatures are shown in Table I. The bulk density (ρ) is shown as the percent theoretical density. Samples sintered at 800 °C had low densities indicating almost no viscous flow or densification. Most of the sintering had occurred at 900 °C, yet a small increase in density was observed at 1100 °C. Densities of samples heat treated at 1300 °C and 1500 °C were lower, probably due to grain growth and grain coarsening before sintering, resulting in entrapment of pores as was seen[2] in the SEM microstructures of the fracture surfaces. At 900 °C, a mixture of hexacelsian and celsian was formed. At all higher temperatures only celsian was detected by XRD. Limited flexural strength measurements were made, and moderate values of 15 - 19 ksi were obtained. Samples that were cold pressed or CIP'ed and HIP'ed crystallized as the monoclinic phase and had densities close to the theoretical value (99.3 and 98.8%, respectively).

In the bulk glass, only by heat treating at temperatures below 1000 °C could pure

hexacelsian be formed. Heat treatment at higher temperatures resulted in the crystallization of celsian. As previously reported[3], with increasing amounts of Ba the hexagonal phase forms at higher temperatures. Although hexacelsian is a metastable phase below the equilibrium transformation temperature of 1590 °C in the Ba analogue, it is the first phase to form at all temperatures. The transformation of the metastable hexacelsian into the stable celsian in the Ba analogue is very sluggish and readily occurs only in the presence of an additive.

Heat treatment of SAS glass flakes at 900 °C for 10 h resulted in pure hexacelsian. This material was used for the hexacelsian-to-celsian transformation kinetics study. XRD patterns of mixtures of the hexacelsian and celsian of various ratios were also calculated using structure factors and unit cell parameters. The calculated and measured XRD patterns were in good agreement.

The results of the heat treatment of hexacelsian flakes are shown in Figure 2 as Avrami plots, $\ln[-\ln(1-x)]$ vs. $\ln t$, where x is the volume fraction transformed after time, t. At temperatures below 1025 °C the transformation was too sluggish and above 1200 °C the rate was very fast. Thus, it was feasible to study the kinetics only within the temperature range reported. The slope of each curve is n, the Avrami constant, which is indicative of the reaction mechanism, and the intercept is $n \ln k$ where k is the reaction rate constant. Values of n and k, at various temperatures are shown in Table II. The plot of $\ln k$ vs. $1/T$ (Figure 3) was a straight line with a slope of E/R, where E is the activation energy and R the gas constant, and an intercept of $\ln \nu$, where ν is the frequency factor. From a linear least squares fit, E was determined to be 125 kcal/mole or 523 kJ/mole and $\nu = 2.88 \times 10^{15}$/s.

An average value of $n = 1.1$ suggests a diffusionless transformation in which a plate grows in one dimension[6]. The transformation of the plate-like structure of the hexacelsian, with no compositional change required, is consistent with such a transformation mechanism. The measured activation energy for the hexacelsian-to-celsian transformation of 125 kcal/mole is somewhat larger than the Si-O bond strength of 109 kcal/mole. The transformation of the layered hexagonal structure to a three-dimensional network structure of the monoclinic phase, similar to feldspars, would necessitate the breaking of the strongest

bonds, the Si-O bonds. Thus a value greater than this bond energy would be expected for the activation energy. Our value of E is not in agreement with Bahat's[7] value of 20 kcal/mole for the same transformation in $BaAl_2Si_2O_8$. We believe that his data are in error and not consistent with a mechanism required to transform the hexagonal to the monoclinic phase. The fact that no thermal event corresponding to the phase transformation was detected during a DSC scan or an isothermal hold is most likely due to a small difference in enthalpy resulting from similar coordination numbers and bond distances in the two structures.

SUMMARY AND CONCLUSIONS

Metastable hexacelsian crystallizes in bulk $SrAl_2Si_2O_8$ glass at temperatures below 1000 °C. At higher temperatures, celsian is also formed. An activation energy of 125 kcal/mole was determined for the hexacelsian-to-celsian transformation in bulk $SrAl_2Si_2O_8$ which is consistent with a mechanism involving the breaking of Si-O bonds. The Avrami constant was determined to be 1.1 suggesting a one-dimensional, diffusionless transformation. The hexacelsian-to-celsian transformation is much faster in the Sr system than in the Ba analogue making it much easier to prepare single-phase celsian in the Sr system. Thus, the Sr-system may be more suitable for use as a high-temperature material.

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Table I. Values of Avrami Constant, n, and Rate Constant, k, for Hexacelsian-to-Celsian Transformation in Bulk $SrAl_2Si_2O_8$ at Various Temperatures

Temperature (°C)	k x $10^6 (s^{-1})$	n
1026	2.55	1.28
1050	6.41	0.94
1100	38.4	0.94
1152	220	1.13
1200	729	1.42

Table II. Properties of Cold Pressed, CIP'ed (60 ksi), and Sintered Glass Bars of $SrAl_2Si_2O_8$ Composition

Heat Treatment	ρ	Phase	σ
800 °C, 20 h	66	g	0.59
900 °C, 20 h	98	H>C,g	2.5
900 °C, 10 h 1300 °C, 10 h	94	C	16
900 °C, 10 h 1300 °C, 20 h	92	C	17
1100 °C, 20 h	97	C	15
1300 °C, 20 h	93	C	19
1500 °C, 20 h	88	C	15

ρ = % Theoretical density (3.084 g/cm^3),
g - glass, H - Hexacelsian, C - Celsian,
σ - Average bend strength (ksi) from 3 test samples

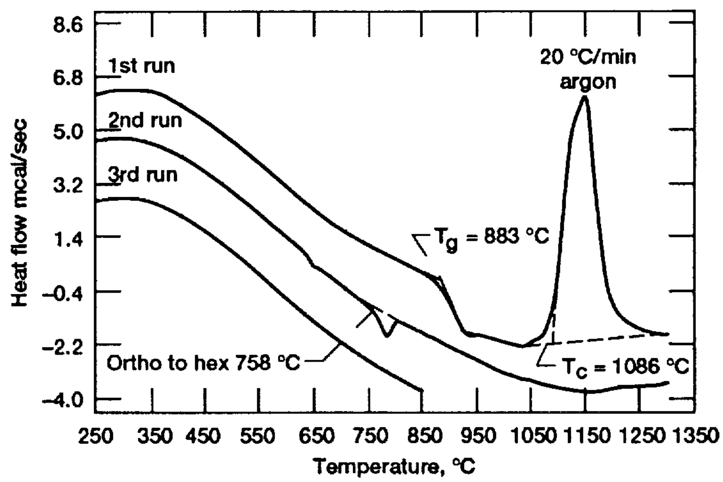

Figure 1.—Repeated DSC scans of bulk $SrAl_2Si_2O_8$ glass. T_g is the glass transition temperature and T_c is the crystallization onset temperature.

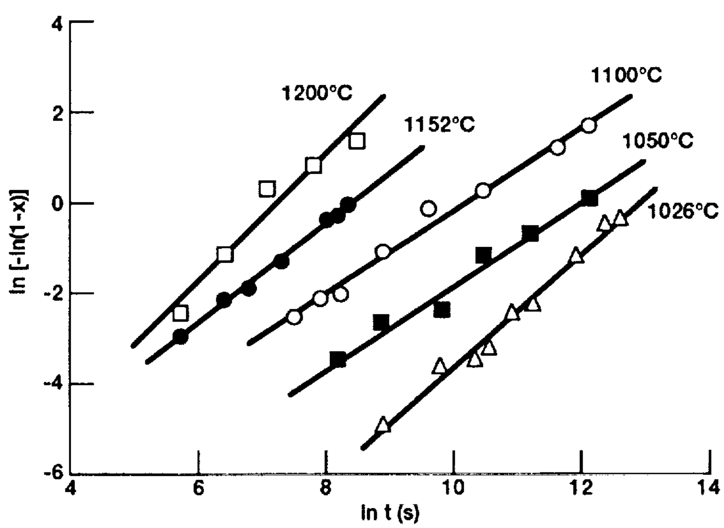

Figure 2.—Avrami plots at various temperatures for hexacelsian-to-celsian phase transformation in bulk $SrAl_2Si_2O_8$.

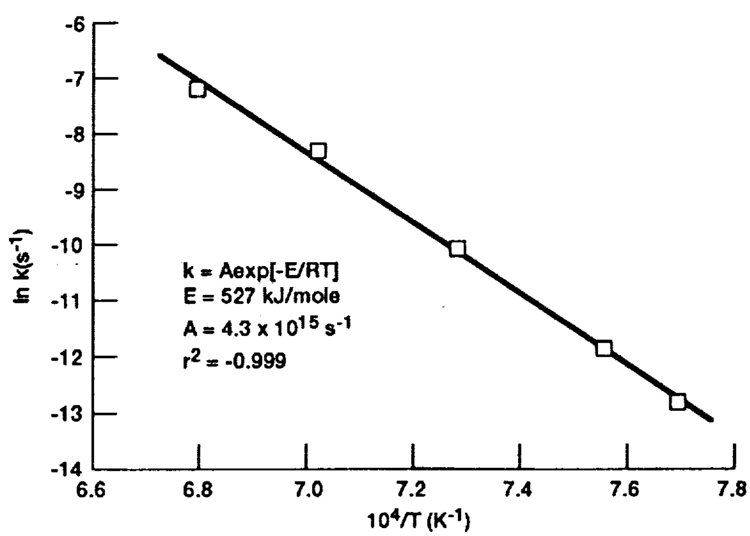

Figure 3.—Arrhenius plot showing temperature dependence of reaction rate constant for hexacelsian-to-celsian phase transformation in bulk $SrAl_2Si_2O_8$.

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13. ABSTRACT ***(Maximum 200 words)***

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